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## EUROPEAN PATENT APPLICATION

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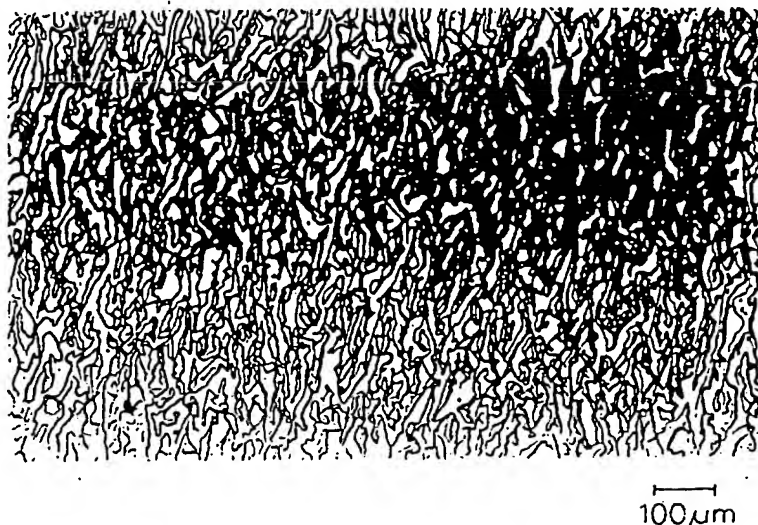
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(54) Ceramic composite material.

(57) A ceramic composite material consisting of single crystal  $\alpha$ - $\text{Al}_2\text{O}_3$  and single crystal  $\text{Y}_3\text{Al}_5\text{O}_{12}$  is provided. This composite material has high mechanical strength and creep behavior particularly at high temperatures.

Fig. 3



100 μm

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## BACKGROUND OF THE INVENTION

## 1. Field of the Invention

5 The present invention relates to a ceramic composite material which has a high mechanical strength and an excellent creep resistance in a wide temperature range from room temperature to high temperature and is suitable to be used as a structural material at a high temperature.

## 2. Description of the Related Art

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SiC or  $\text{Si}_3\text{N}_4$  has been investigated to develop ceramic materials to be used at high temperatures but is not sufficient in high temperature properties. As an alternative material thereof, SiC:SiC composite materials produced by chemical vapor impregnation, provided by Societe Europeene de Propulsion, have attracted attention, at the present are considered to be the best high temperature structural materials and have been

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investigated and developed. The temperature range at which they can be used is reported to be 1400 °C or lower.  
Mr. T. Parthasarathy et al. in Journal of the American Ceramics Society Vol. 76, No. 1, pp29 - 32 (1993) disclosed a composite of alumina and yttrium aluminum garnet (sometime hereinafter referred to as "YAG") of eutectic  $\text{Al}_2\text{O}_3$ - $\text{Y}_3\text{Al}_5\text{O}_{12}$ . Mr. Parthasarathy et al. also disclose a method of producing the composite by

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unidirectionally melting and solidifying a mixed powder of  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  in a crucible.  
It is comprehensible from the description on page 29, right column, lines 9 to 10 and Figs. 1 and 2 of the literature that the composite is polycrystalline and includes grain boundaries. This is clearly supported from the description "The failure was usually along the colony boundaries with crack running along the  $\text{Al}_2\text{O}_3$ -YAG interface boundaries". These colony boundaries are shown as portions where the microstructure

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is larger than in the other portions in Fig. 2 of the literature.  
This composite material has stresses equivalent to those of sapphire at 1530 °C and 1650 °C when the strain rate was make constant.

Moreover, the present inventors confirmed in experiments that the composite disclosed by Mr. Parthasarathy et al. includes pores or voids in the microstructure and the mechanical strength of the

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composite rapidly lowers at high temperature.  
Therefore, the object of the present invention is to provide a ceramic composite material comprising sapphire, single crystalline  $\alpha$ - $\text{Al}_2\text{O}_3$ , and YAG, which has an excellent mechanical strength and creep behavior from room temperature to high temperature and significantly improved these properties particularly at high temperature.

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## SUMMARY OF THE INVENTION

The above object is attained in accordance with the present invention by providing a composite material consisting essentially of single crystal  $\alpha$ - $\text{Al}_2\text{O}_3$  and single crystal  $\text{Y}_3\text{Al}_5\text{O}_{12}$ .

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## BRIEF DESCRIPTION OF THE INVENTION

Figs. 1 and 2 are X-ray diffraction patterns of the composite material obtained in Example 1;

Fig. 3 is a photomicrograph of the composite material of Example 1;

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Fig. 4 is an X-ray diffraction pattern of the composite material obtained in Comparative Example 1; and

Fig. 5 is a photomicrograph of the composite material of Comparative Example 1.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

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The term "single crystal" used in the specification means the crystal structure in which only a diffraction peak from a certain crystal plane of  $\alpha$ - $\text{Al}_2\text{O}_3$  or  $\text{Y}_3\text{Al}_5\text{O}_{12}$  is observed in an X-ray diffraction of the composite material.

Fig. 1 is an X-ray diffraction pattern from a plane perpendicular to the solidification direction of the ceramic composite material prepared in Example 1, described later, and Fig. 2 is an X-ray diffraction pattern from a plane declined by about 76° from the solidification direction of the same ceramic composite material (no diffraction peak of  $\text{Al}_2\text{O}_3$  was obtainable from an angle perpendicular to the solidification direction).

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Fig. 1 shows only a peak at  $2\theta = 33.26^\circ$  corresponding to diffraction from (420) plane of YAG. Fig. 2 shows only a peak at  $2\theta = 37.78^\circ$  corresponding to diffraction from (110) plane of  $\text{Al}_2\text{O}_3$ . These facts clearly indicate that the ceramic composite material of the present invention consists of single crystal  $\alpha\text{-Al}_2\text{O}_3$  and single crystal YAG.

Fig. 4 is an X-ray diffraction pattern from an angle perpendicular to the solidification direction of the ceramic composite material prepared in Comparative Example 1. Fig. 4 shows diffraction peaks from (110) plane of  $\text{Al}_2\text{O}_3$  and (420) plane of YAG, as above, as well as the following peaks: for  $\text{Al}_2\text{O}_3$ , diffraction peaks at  $2\theta = 26.62^\circ$ ,  $52.7^\circ$  and  $59.78^\circ$  corresponding to (012), (024) and (211) planes respectively and for YAG, diffraction peaks at  $2\theta = 18.1^\circ$ ,  $27.8^\circ$ ,  $29.78^\circ$ ,  $36.64^\circ$ ,  $38.22^\circ$ ,  $41.18^\circ$ ,  $46.62^\circ$  and  $60.7^\circ$  corresponding to (211), (321), (400), (422), (431), (521) (532) and (651) planes respectively. This X-ray diffraction clearly indicates that the ceramic composite material obtained in Comparative Example 1 was polycrystalline.

The fact that the ceramic composite material of the present invention consists of single crystal  $\alpha\text{-Al}_2\text{O}_3$  and YAG and is obviously different from the composite materials obtained by Mr. Parthasarathy et al. and in Comparative Example 1, is also supported by Fig. 3 showing a photomicrograph of the ceramic composite material obtained in Example 1. In the photomicrograph shown in Fig. 3, no colony, grain boundary or coarse grain is observed, in contrast to Figs. 1 and 2 of Mr. Parthasarathy et al.'s literature. This photomicrograph corresponds well to the result of the X-ray diffraction indicating that the ceramic composite material consists of single crystal  $\alpha\text{-Al}_2\text{O}_3$  and single crystal YAG.

Fig. 5 is a photomicrograph of the ceramic composite material obtained in Comparative Example 1. Fig. 5 shows that the ceramic composite material includes colonies, grain boundaries or coarse grains, and pores or voids, as shown in Mr. Parthasarathy et al.'s literature.

It is proved from comparison between Figs. 1 and 2 and Fig. 4 and comparison between Fig. 3 and Fig. 5 that the ceramic composite material of the present invention is a novel composite material consisting of single crystal  $\alpha\text{-Al}_2\text{O}_3$  and single crystal YAG, different from the composite material disclosed by Mr. Parthasarathy et al.

In the ceramic composite material of the present invention, the single crystal  $\alpha\text{-Al}_2\text{O}_3$  and single crystal YAG form a uniform sea/island structure when a cross-sectional microstructure is observed. It is not certain but is considered that the sea is single crystal  $\alpha\text{-Al}_2\text{O}_3$  and the island is single crystal YAG. The sizes of the sea and islands may be varied and controlled by selecting the solidification conditions, but are typically in a range of 10 to 50  $\mu\text{m}$ .

The amounts of single crystal  $\alpha\text{-Al}_2\text{O}_3$  and single crystal YAG in the composite material of the present invention can be varied in ranges of about 20 to 80% by volume of single crystal  $\alpha\text{-Al}_2\text{O}_3$  and about 80 to 20% by volume of single crystal YAG, by changing the proportion between the  $\text{Al}_2\text{O}_3$  and YAG starting powders. The eutectic composition is 55% by volume of  $\text{Al}_2\text{O}_3$  and 45% by volume of YAG.

The ceramic composite material of the present invention can be produced; for example, by the following process.

A mixed powder of  $\alpha\text{-Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  powders in a ratio for a desired ceramic composite material is prepared by weighing and mixing. The mixing method is not particularly limited and may be either of a dry mixing method or a wet mixing method. In a wet mixing method, alcohol such as methanol and ethanol is generally used as a medium.

The mixed powder is then heated to a temperature at which both starting powders are molten, for example, at 1800 to 2500  $^\circ\text{C}$ , in a conventional furnace, for example, an arc furnace to melt the mixed powder.

Subsequently, the melt is charged in a crucible and then unidirectionally solidified to prepare a ceramic composite material of the present invention. Alternatively, the melt is once solidified and crushed and the crushed material is then charged in a crucible and melted and unidirectionally solidified.

The atmospheric pressure during the melting and solidification is generally  $10^{-3}$  Torr or less, preferably  $10^{-4}$  Torr or less. The speed of moving the crucible for unidirectional solidification, i.e., the rate of growth of the ceramic composite material is generally 50 mm/hour or less, preferably 1 to 40 mm/hour. The control of the conditions other than the atmospheric pressure and crucible moving speed can be done in the same manner as in conventional methods.

If the atmospheric pressure or the crucible moving speed during the melting and solidification is outside the above ranges, the material may become polycrystal line, pores or voids tend to appear at colony boundaries, and it is difficult to obtain a composite material excellent in mechanical strength and creep behavior.

The apparatus for unidirectional solidification may be a conventional one in which a crucible is vertically movably mounted in a vertically arranged cylindrical container, an induction heating coil is disposed around the approximate center position of the cylindrical container, and a vacuum pump is provided to evacuate the

container space.

## EXAMPLES

### 5 Example 1

$\alpha$ - $\text{Al}_2\text{O}_3$  powder (Sumitomo Chemical Co., Ltd., AKP-30) and  $\text{Y}_2\text{O}_3$  powder (Shin-etsu Chemical Co., sub-micron type) in a molar ratio of 82% of the former to 18% of the latter were milled in a wet ball mill using ethanol. The obtained slurry was dried in a rotary evaporator to remove ethanol.

10 The obtained mixed powder of  $\alpha$ - $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  was charged in a crucible placed in a chamber, in which the atmospheric pressure was maintained at  $10^{-5}$  Torr and the crucible was heated by an induction coil to 1850 to 1900 °C to melt the mixed powder in the crucible. Subsequently, unidirectional solidification was conducted by descending the crucible at a speed of 5 mm/hour under the above atmospheric pressure to obtain a ceramic composite material.

15 Figs. 1 and 2 show X-ray diffraction patterns of the composite material obtained from planes perpendicular to and declined by about 76° from the solidification direction of the composite material. Only a diffraction peak from (420) plane of single crystal YAG is observed in Fig. 1 and only a diffraction peak from (110) plane of single crystal  $\alpha$ - $\text{Al}_2\text{O}_3$  is observed in Fig. 2, which demonstrates that the above composite material consists of single crystal YAG and  $\alpha$ - $\text{Al}_2\text{O}_3$ .

20 Fig. 3 is a photomicrograph of the composite material. Fig. 3 demonstrates that the composite material does not include any colony or grain boundary, pores or voids do not exist, and a uniform sea-island structure is formed.

The mechanical strengths of the composite material are shown in Table 1, where the three point bending strength and compressive creep property were measured in air.

### 25 Comparative Example 1

The procedures in Example 1 were repeated except that the atmospheric pressure in the chamber was normal pressure to obtain a ceramic composite material. The X-ray diffraction pattern and optical micro-  
30 scopic photograph of the obtained composite material are shown in Figs. 4 and 5.

Fig. 4 shows diffraction peaks from (012), (024), (110) and (211) planes of  $\text{Al}_2\text{O}_3$  and diffraction peaks from (211), (321), (400), (420), (422), (431), (521), (532) and (651) of YAG, indicating that the composite material is a polycrystal. Fig. 5 demonstrates that the composite material includes colony or grain boundary phases and pores.

35 The mechanical strengths of this composite material are also shown in Table 1. Table 1 also includes the mechanical properties of the sapphire fiber from Journal of the American Ceramic Society Vol. 63, No. 7, pp429 - 435.

Table 1

	Example 1	Comparative Example 1	Sapphire fiber
Three point bending strength (MPa)			
at 1400 °C	490	350	-
at 1500 °C	490	320	-
at 1600 °C	410	250	-
at 1700 °C	370	210	-
Compressive creep strength at 1600 °C (MPa):			
at Strain rate $1 \times 10^{-4} \text{ sec}^{-1}$	450	270	280
at Strain rate $1 \times 10^{-5} \text{ sec}^{-1}$	370	210	220

### 55 Claims

1. A ceramic composite material essentially consisting of single crystal  $\alpha$ - $\text{Al}_2\text{O}_3$  and single crystal  $\text{Y}_3\text{Al}_5\text{O}_{12}$ .

2. A ceramic composite material according to claim 1 wherein said composite material comprises 20 to 80% by volume of the single crystal  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and 80 to 20% by volume of the single crystal Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>.
3. A ceramic composite material according to claim 1 wherein said single crystal  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and said single crystal Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> form a uniform sea-island structure in which sea and islands have a size of 10 to 50  $\mu$ m.
4. A ceramic composite material according to claim 1 wherein said composite material does not include colony, grain boundary pores and voids.

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Fig.1

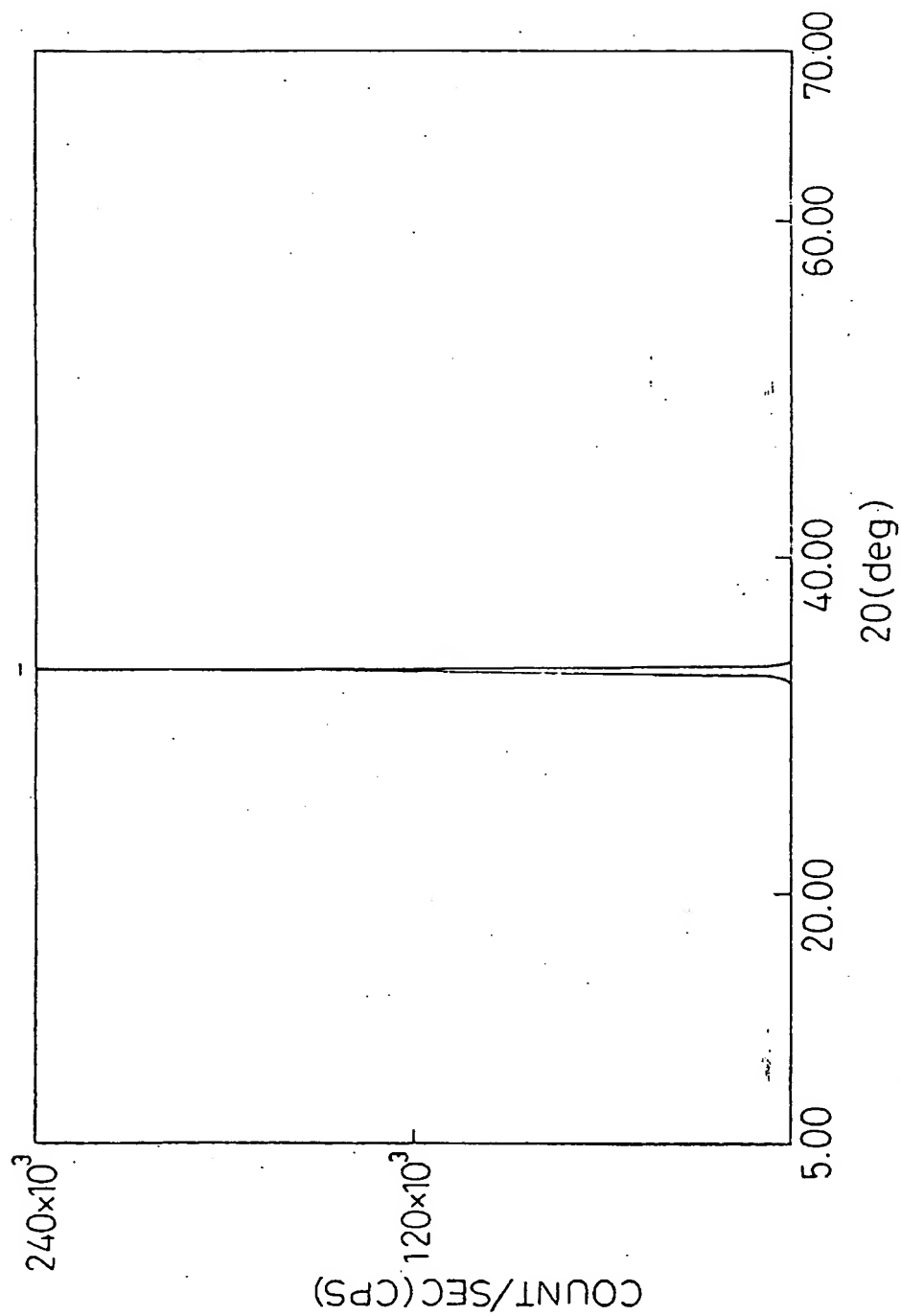


Fig.2

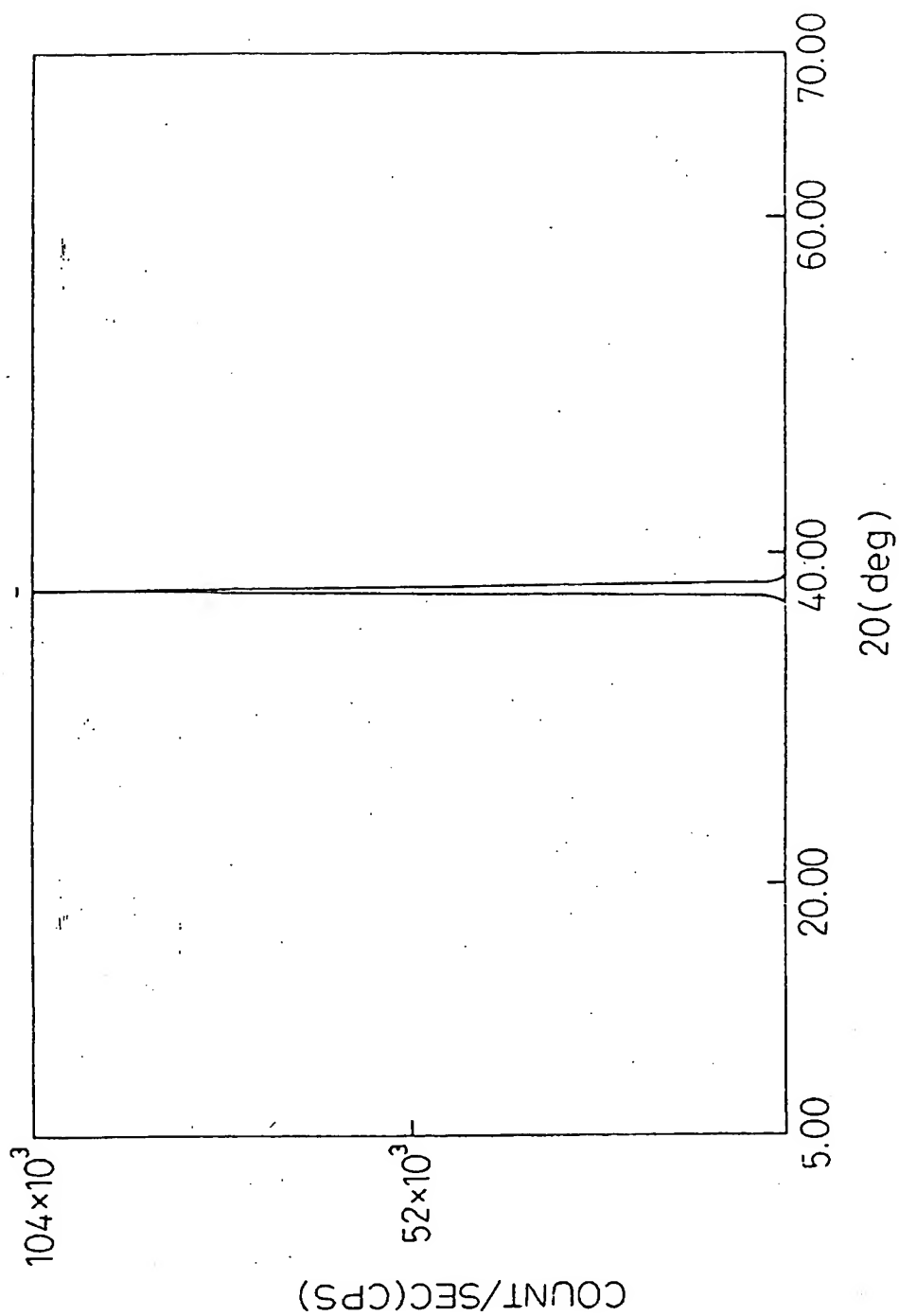
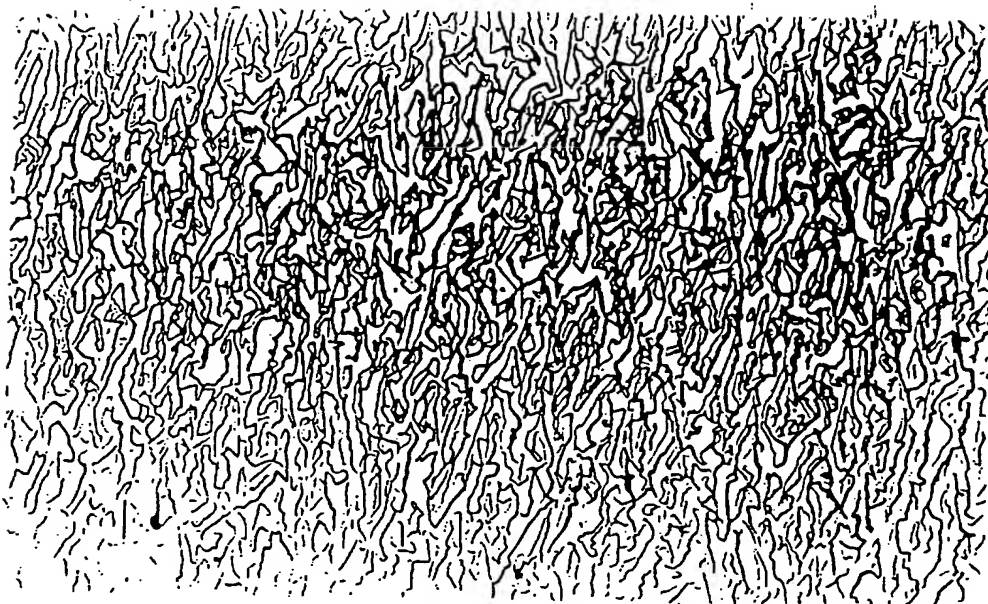


Fig. 3



100  $\mu$ m



Fig. 4  
PRIOR ART

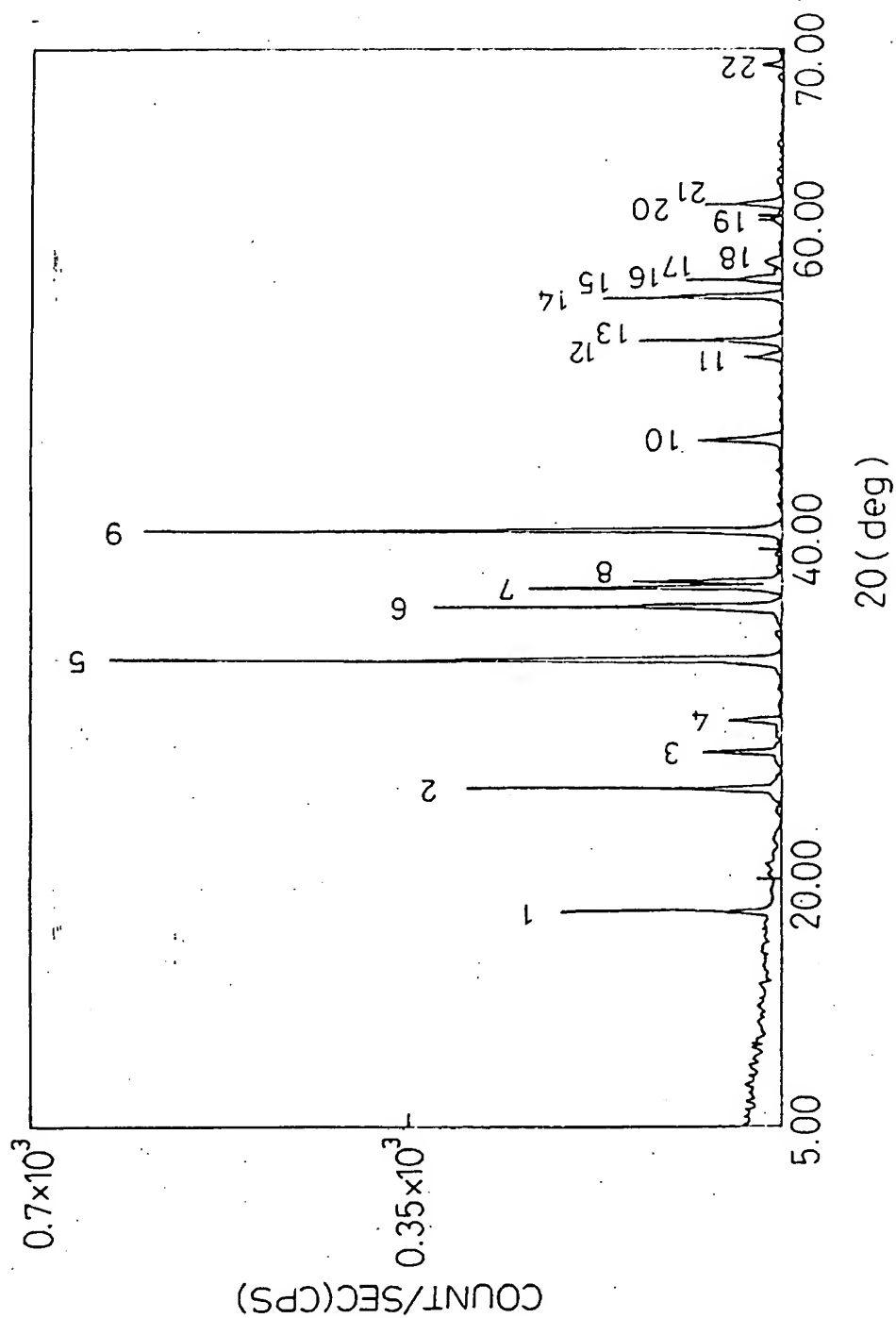


Fig. 5



100  $\mu$ m



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## EUROPEAN SEARCH REPORT

Application Number  
EP 94 11 5796

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 6)
A, D	J. AMERICAN CERAMIC SOCIETY, vol. 76, no. 1, 1993 pages 29 - 32 T. PARTHASARATHY * the whole document *	1-4	C04B35/117 C04B35/44 C30B11/00
			TECHNICAL FIELDS SEARCHED (Int. Cl. 6)
			C04B C30B
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 24 January 1995	Examiner Luethé, H
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document	

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Fig.1

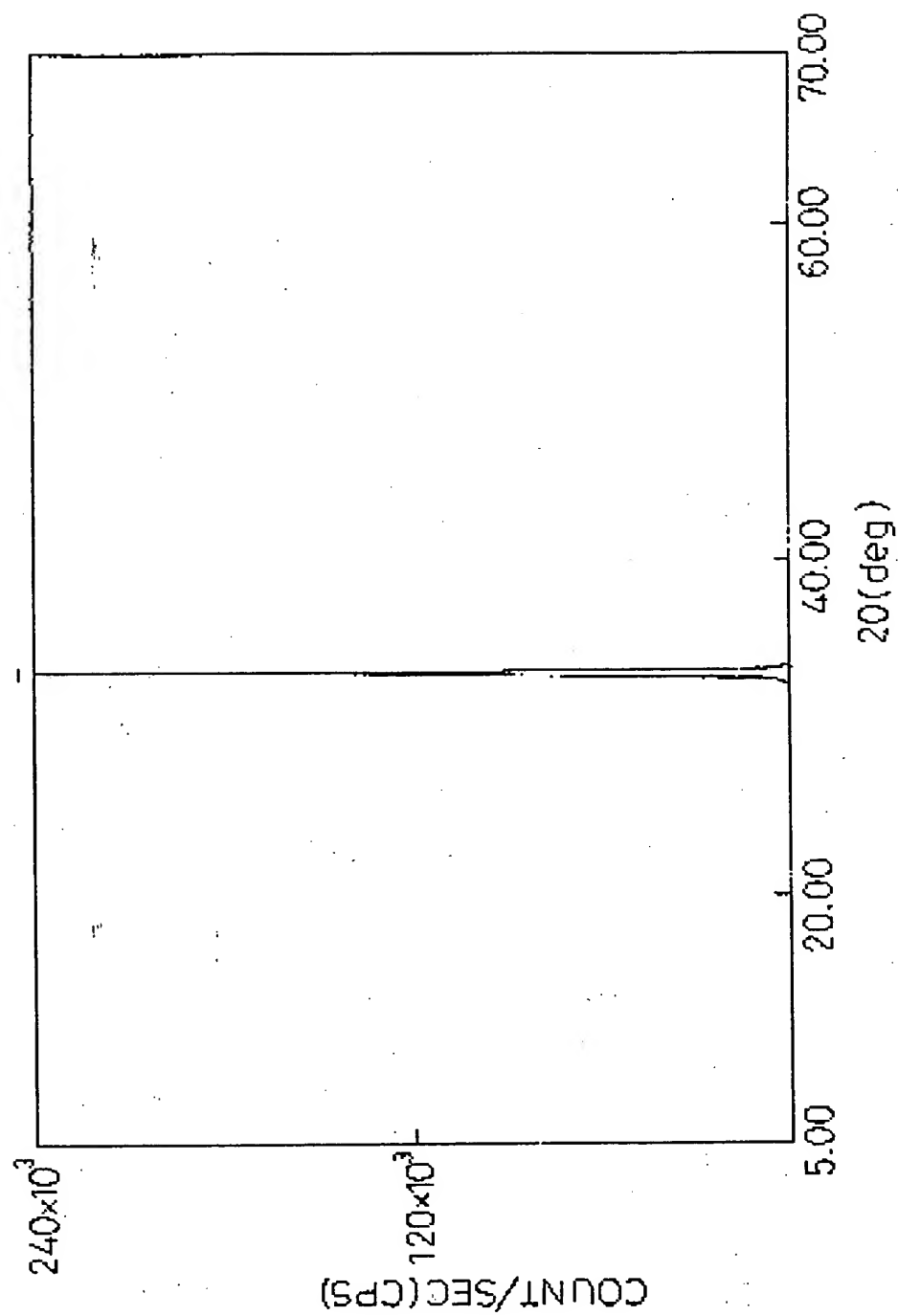


Fig.2

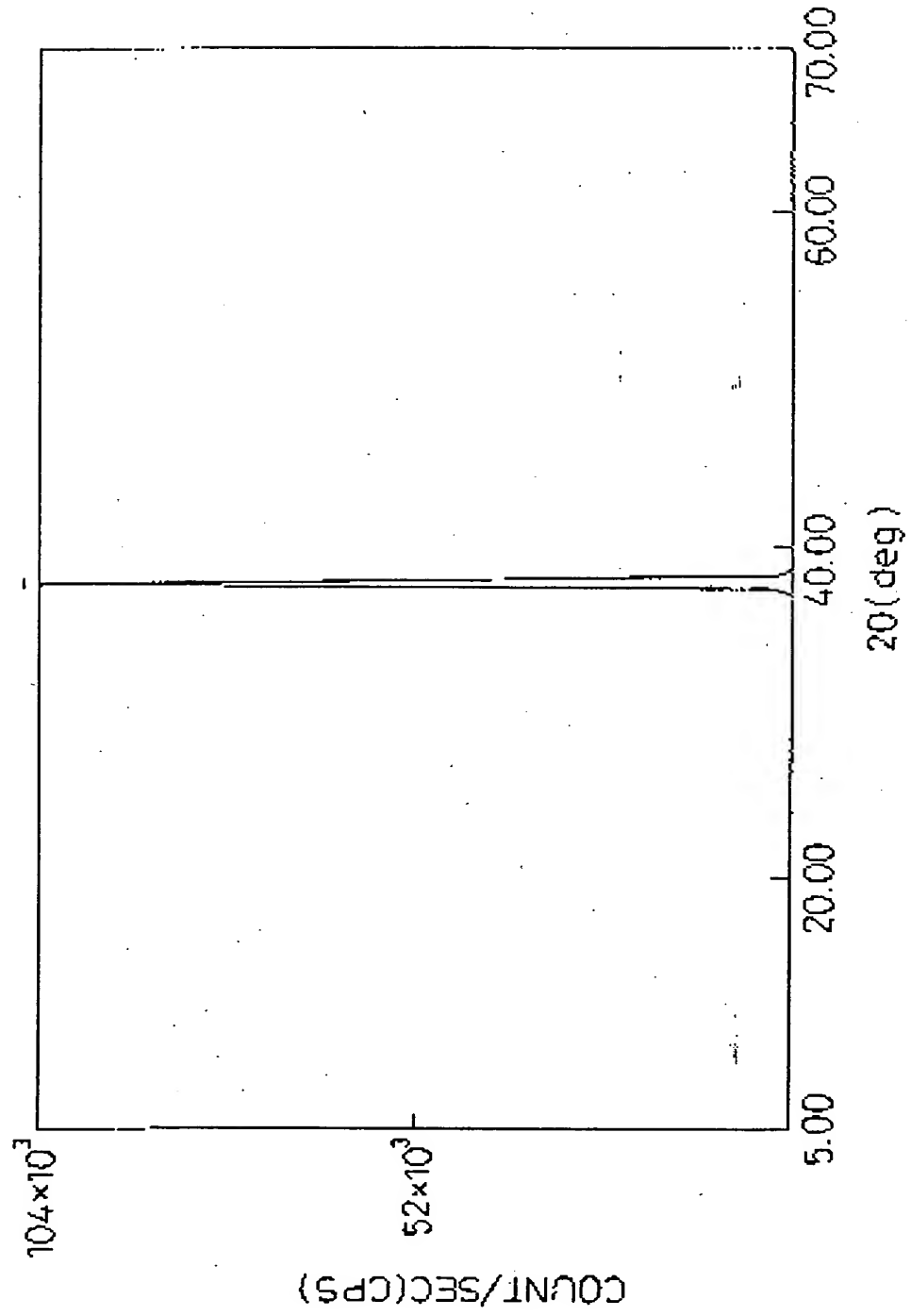
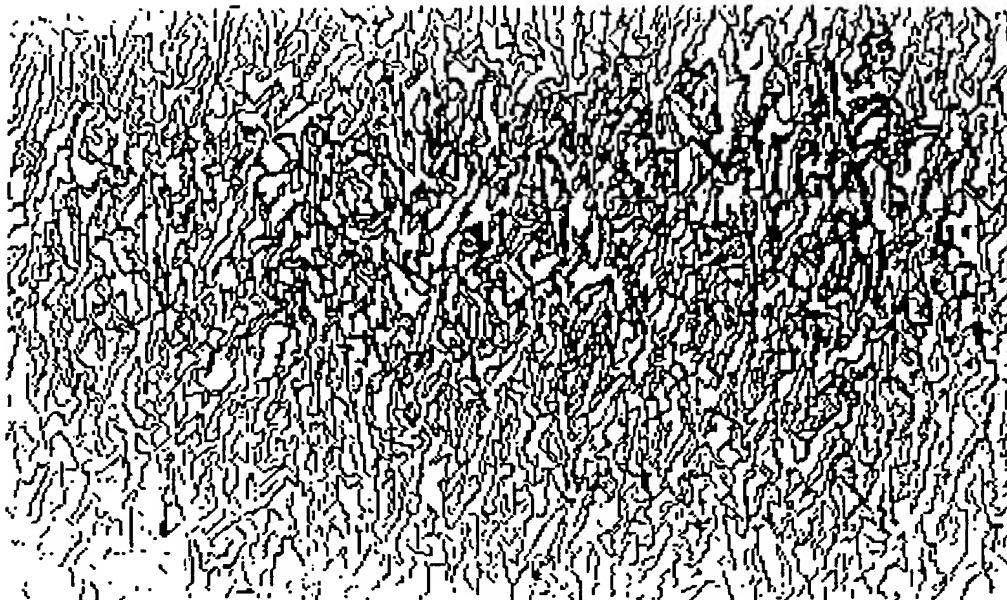


Fig. 3



100µm

Fig. 4  
PRIOR ART

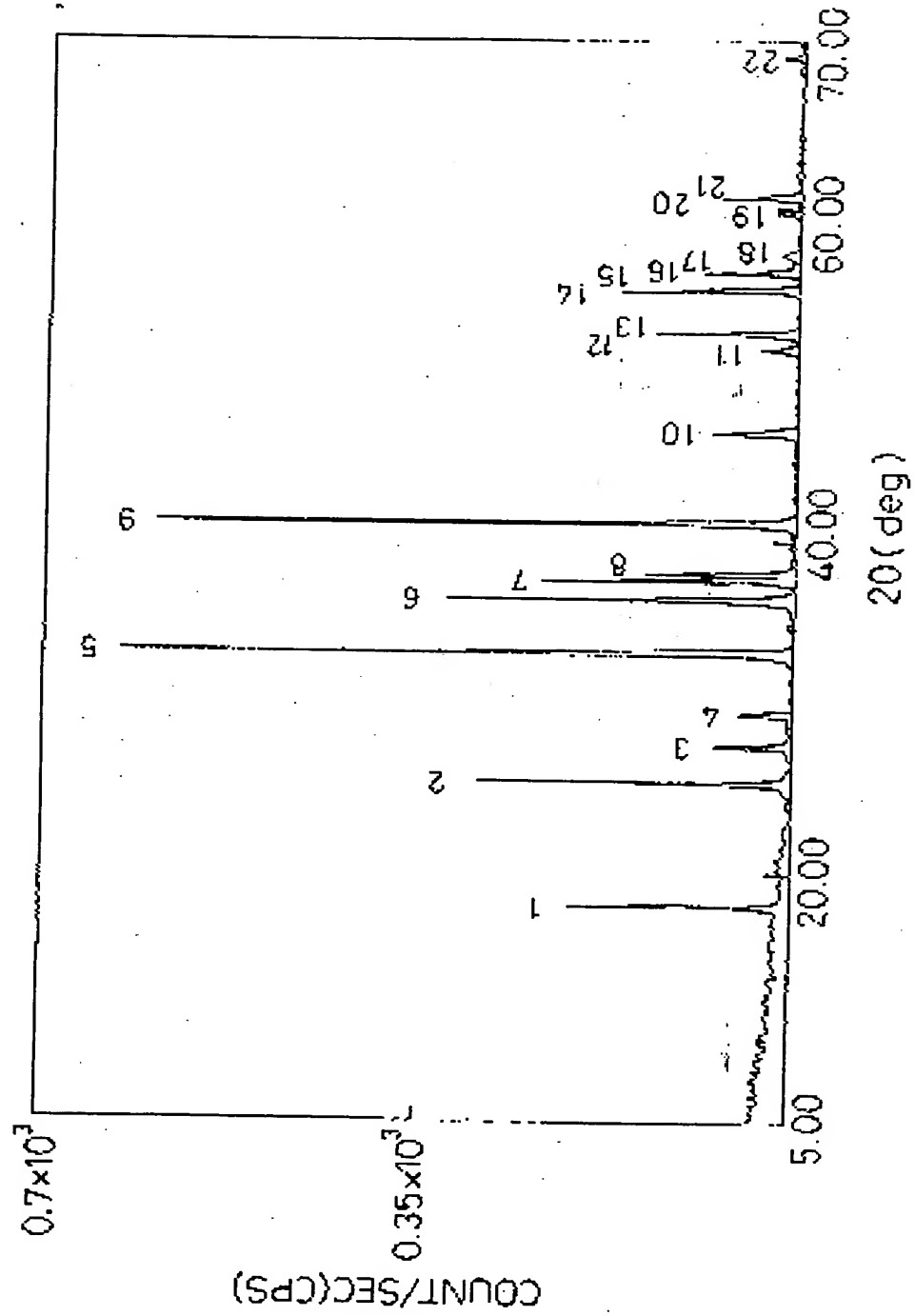




Fig. 5



100  $\mu$ m

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